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(54) **Wax conversion process.**

(57) Hydrocarbon lube boiling range stock of high Pour Point may be catalytically hydrotreated to yield a product of high viscosity index and reduced Pour Point which is suitable as a lube base oil. The catalyst comprises a non-noble Group VIII metal, a Group VI B metal, optionally phosphorus and halogen. The catalyst is used at 280°-500°C, a pressure of 2-33 kPa gauge, LHSV of 0.1-10 and hydrogen feed rate of 88-1800 m³/m³.

This invention relates to a wax conversion process. More particularly it relates to a process for converting a waxy hydrocarbon feedstock of high pour point to a hydrocarbon product of reduced wax content and high viscosity index which is particularly suitable for use as an automatic transmission fluid, premium motor oil, etc. The product oil is particularly characterized by very good low temperature properties and by a high viscosity index.

As is well known to those skilled in the art, suitable heavier hydrocarbons may be employed as charge stock for various products including lubricating oils, automatic transmission fluids. Commonly, however, it is found that the charge stocks need considerable processing in order to make them suitable as a base oil for such uses. Various processes may be employed to convert these charge oils into base stocks characterized by decreased wax content, decreased pour point, decreased aromatics content.

There is a large body of literature and patents which address this area. Typical of these are the following:

Bijward, H. M. J. et al The Shell Hybrid Process, an Optimized Route for HVI (High Viscosity Index) Lube oil Manufacture paper from Pet. Ref. Conf. of the Jap. Pet. Inst 27-28 October 1986, p16;

Bulls, S. et al Lube oil Manufacture by Severe Hydrotreatment Proc. Tenth World Pet. Congress Vol 4, 1980 p221-8.

US 3,268,439
US 3,658,689
US 3,764,516
US 3,830,723
US 4,547,283
US 4,900,711
US 4,911,821

EP 0 321 299
EP 0 321 302
EP 0 335 583

GB 1,098,525
Continuing studies are in progress in an attempt to improve the quality of base stocks so that they may be employed as premium motor oils and transmission fluids. There is also a need to process sulfur-containing charge to prepare satisfactory product - without hydrotreating. It is also found that there is a need to treat charge stock such as slack wax, typically containing substantial content of sulfur (above 100 ppm) and paraffins in order to permit attainment of product oils (suitable for such desired uses) characterized by high viscosity index (typically 120-150) and reduced or low pour point at mid-range viscosity (typically \leq 300 SUS @ 38°C).

It is an object of this invention to provide a process for treating a waxy hydrocarbon such as slack wax to convert it into a product oil containing decreased content of normal paraffins and increased content of isoparaffins.

In accordance with certain of its aspects, this invention is directed to a process for converting a waxy hydrocarbon charge of high Pour Point and containing

sulfur and paraffins to a hydrocarbon product, of reduced Pour Point and high viscosity index, suitable for use as a lube oil base stock which comprises

maintaining a bed of sulfur-tolerant supported catalyst containing a non-noble Group VIII metal, a Group VI B metal, optionally phosphorus and halogen, having a Total Surface Area of 100-250 m²/g and a pore size distribution as follows:

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Pore Size	Pore Volume cc/g
< 100 Å	0.20-0.50
100-160 Å	0.01-0.05
> 160 Å	0.01-0.10

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and a Pore Mode of 60Å-100Å diameter;

passing waxy hydrocarbon charge of high Pour Point and containing sulfur and paraffins to said bed of catalyst;

maintaining said bed of catalyst at wax conversion conditions including temperature of 288-482°C (550°F-900°F), pressure of 2-33 kPa g.p. (300-5000 psig), space velocity LHSV of 0.1-10, and hydrogen feed rate of 88-1800 m³/m³ (500-10,000 SCFB) thereby converting said waxy hydrocarbon charge to a hydrocarbon

product, of reduced Pour Point and high viscosity index; and
recovering said hydrocarbon product.

The waxy hydrocarbon charge which may be treated by the process of this invention includes those which are particularly characterized by a high content of wax - typically at least about 40% and commonly above 55w% paraffins. These charge compositions contain 40-95w%, commonly 55-95w%, say 85w% paraffins. They may also be characterized by a high pour point - typically above about 80°F, commonly 80°F-120°F, say 90°F. In the case of slack wax, the pour point may be even higher - say up to 150°F. These stocks may commonly contain sulfur in amount of > 100 wppm i.e. greater than 0.01w%.

These charge hydrocarbons may typically be obtained as side streams from a vacuum tower; and they will commonly not have been subjected to further processing. Charge compositions may also include slack wax or petrolatum recovered from a dewaxing operation, soft wax, wax distillates recovered from non-lube waxy crudes (e.g. Minas, Altamont). Other possible feedstocks may include raffinates from solvent refining of high wax content wax distillates including those recovered during refining with N-methyl pyrrolidone-2, furfural and phenol. It is also possible to treat soft waxes obtained from deoiling of (i) slack wax, (ii) high wax content distillates or (iii) deasphalted oil. Solvent extracted streams such as distillates or deasphalted oils may be treated by the process of this invention.

It is a feature of the process of this invention that it is particularly adapted to permit operation with non-conventional charge containing much higher wax content (e.g. ≥ 40w%) than is present in conventional charge to hydrotreating - which latter charge commonly contains less than about 30w% wax.

Illustrative specific waxy hydrocarbon charge stocks which may be treated by the process of this invention may include the following:

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TABLE

Test	<u>A</u>		<u>B</u>		<u>C</u>		<u>D</u>		<u>E</u>		<u>F</u>		<u>G</u>	
	Unrefined Minas 7		Unrefined Minas 8		Solvent Ref. Minas 8		Slack Wax 20		Slack Wax 40		Petrolatum		Soft Wax	
	<u>Dist.</u>	<u>Dist.</u>	<u>Dist.</u>	<u>Dist.</u>	<u>Dist.</u>	<u>Dist.</u>	<u>Dist.</u>	<u>Dist.</u>	<u>Dist.</u>	<u>Dist.</u>	<u>Dist.</u>	<u>Dist.</u>	<u>Dist.</u>	<u>Dist.</u>
API Gravity	35.0	31.9	33.0	38.0	36.4	31.4	34.8							
Nitrogen, ppm	344	458	56.6	18.1	29.8	231	28.4							
Sulfur, wt%	0.08	0.2	0.102	0.05	0.37	0.32	0.026							
Wax Content, wt%	49.0	45.5	50.4	89.1	87.1	88.5	41.5							
Vis.Kin.cst @65.6°C	8.24	13.18	11.28	11.00	18.26	53.47	14.3							
100°C	4.01	5.76	5.24	5.36	6.19	19.17	6.23							
VII visc., sus @100°F	129	125	146	179	175	141	132							
	93	163	133	119	211	803	176							
IBP	548	559	556	654	513	790	668							
10%	687	776	773	786	870	931	775							
50%	792	848	850	881	968	1037	877							
90%	863	897	902	973	1031	1118	952							
EP	923	948	1336	1059	1116	1178	1169							

It is a feature of the process of this invention that it may be carried out in one or more separate beds in

one reactor or in several reactors. In the case of wax distillate charge, the reaction may be carried out in two or more beds after the first of which, diluent (e.g. hydrogen or additional charge hydrocarbon) may be admitted to control the exotherm i.e. to maintain the temperature of the reaction mixture within the noted range. In the case of e.g slack wax, the exotherm is not normally so large as to require inter-bed cooling or addition of diluent.

- 5 The supported catalyst which may be employed in the process of this invention may contain 2-10w% non-noble Group VIII metal, 5-30w% Group VI B metal, 0-2w% phosphorus, and 0-10w% halogen. The total metal content may be 10w%-35w%, preferably 20w%-30w%, say 25w% of the support. The atomic ratio of Group VIII metal to Group VI B metal is preferably 0.5-2:1, more preferably 0.5-1.5:1, typically 0.75-1.25, say about 1:1.
- 10 The supported catalyst may contain 0-10w% halogen preferably 0.5-10w%, more preferably 0.5-7w%, typically 0.5-5w%, say about 2w%. Phosphorus may be present in amount of 0-2w%, say 0w%.
The support typically may contain 0.5-15w%, say 15w% silica and 85-99.5w%, say 85w% alumina.
The catalyst which may be employed in the process of this invention may be a sulfur-tolerant supported (on 15% silica/85% alumina support) catalyst containing:
- 15 (i) a non-noble Group VIII metal (Fe, Co, or Ni) in amount of 2-10w%, preferably 3-8w%, say 6w%
(ii) a Group VI B metal (Cr, Mo, or W) in amount of 5-30w%, preferably 10-25w%, say 19w%
(iii) phosphorus in amount of 0-2w%, preferably 0-2w%, say 0w%
(iv) halogen (Cl, Br, I, or preferably F) in amount of 0-10w%, preferably 0.5-10w%, say 2w%.
- 20 The supported catalyst which may be employed may be formed on a support of silica, alumina, silica-alumina, magnesia, magnesia-alumina, etc by contacting the formed support with an aqueous solution of a water-soluble composition of one component (e.g. Group VIII metal), drying, and calcining followed by contacting with an aqueous solution of a water-soluble composition of another component (e.g. Group VI B metal) drying, and calcining. Haliding may be effected by contacting the support as with an aqueous solution (e.g. of fluosilic acid), drying, and calcining.
- 25 It is preferred, however, to prepare the catalyst by blending the components prior to e.g. extrusion. In this preferred embodiment, the catalyst may be formed by extruding an aqueous mixture (in amounts corresponding to those set forth supra) containing silica, alumina, fluorine (as from fluosilic acid) and when desired phosphorus. The catalyst may then be dried at 100°C-200°C, say about 125°C for 12-24 hours, say about 18 hours and then calcined at 400°C-600°C, say about 500°C for 0.5-4, say 1 hour.
- 30 The catalyst so-prepared is characterized by a Total Surface Area of 100-250 m²/g and a Pore Size Distribution as follows:

TABLE

Pore size	Pore Volume cc/g
< 100Å	0.20-0.50
100-160Å	0.01-0.05
> 160Å	0.01-0.10

35 and a Pore Mode of 60-100Å Diameter

40 Illustrative catalysts which may be employed may be characterized as follows:

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Property	A	B	C	D
Nickel w%	6	3	5	6.5
5 Molybdenum w%		13	15.5	
	19			19.4
	2			3.4
10 SiO ₂	13.5		49	2.5
	45.0	84	38	
	152	162		126
15 A ₁ O ₃	0.42	0.47		0.38
	72			
	20	24	30	15.8
20 Av. Pore Diameter Å	0.063		0.070	0.062
	0.217		0.30	0.13
	61.2	52.5	49.9	62.4

- 25 In practice of the process of this invention, the waxy hydrocarbon charge of high Pour Point and containing at least about 40w% of paraffins is charged to the bed of catalyst. Reaction conditions include temperature of 550°F-900°F, preferably 725°F-800°F, say about 750°F, pressure of 300-5000 psig, preferably about 1000-1500, say about 1000 psig, LHSV of 0.45-0.60, preferably 0.50-0.60, say about 0.5, and hydrogen feed rate of 500-10,000, say 2500 SCFB.
- 30 During contact with catalyst at the conditions of operation, the hydrocarbon charge is subjected to wax conversion reactions the principal one of which appears to be isomerization of normal paraffins to isoparaffins. The degree of conversion may be measured by the decrease in content of material (i.e. wax) which crystallizes out on chilling in the presence of dewaxing solvent as measured by Test Method ASTM D-3235 or ASTM D-721 or ASTM D-1601, as appropriate.
- 35 It is a particular feature of the process of this invention that these improvements may be attained at a high Reaction Yield - typically above about 25w% and commonly 40-60w%, say about 50w%. (Reaction Yield, or wax-free Lube Yield, is defined as the product of the 700°F+ bottoms yield in weight % times the oil content weight fraction).
- 40 In practice of the process of this invention, it is possible to direct the course of the reaction to attain either low Pour Point or high Reaction Yield; although both of these factors may be improved over the noted range of reaction conditions (including temperature, pressure, and space velocity), it is possible by operating at desired points within the range to direct the reaction to permit attainment to greater degree of one or the other of these desiderata. For example, if one is primarily interested in improvement in Pour Point (i.e. production of product of low Pour Point), then operation should typically be carried out to attain product having an oil content above about 80w%.
- 45 Although the conditions to attain this end may be different for different charge stocks, they may preferably include temperature of say 750°F-850°F, pressure of say 400-2400 psig. LHSV of 0.45-0.55 and hydrogen feed rate of 2500 SCFB.
- 50 When it is desired to operate in a manner to attain high Reaction Yield (700°F Wax Free Yield) with satisfactory Pour Point, operation may be carried out to attain product having an oil content below about 80w%, say 70%-80%. The conditions to attain this oil content will vary for different charge stocks - but generally it will mean operation at a temperature of about 20°F-30°F, say 25°F below that at which low Pour Point is attained i.e. at temperature of say 725°F-825°F at essentially the same pressure and space velocity.
- 55 Typical results attained when it is desired to attain product of low Pour Point may be as follows:

55 50 45 40 35 30 25 20 15 10

TABLE

Conditions Reactor	A Unrefined Minas 7 Distillate	B Unrefined Minas 8 Distillate	C Solvent Ref. Minas 8 Distillate	D Slack Wax 20	E Slack Wax 40	F Petrolatum	G Soft Wax
Reactor Temp, F Reactor	826	826	800	771	775	801	775
Pressure, psig	996	997	998	997	1001	998	1008
Space Velocity, LSHV	0.55	0.53	0.55	0.53	0.55	0.55	0.50
Test							
Viscosity, SUS @ 100F	58	66	66	66	89	165	61
Viscosity Index	131	145	130	135	144	171	112
Pour Point, F	25	25	20	25	55	95	0
Reactor Yield, Wt% (700+F)	23.3	24.2	29.3	40.4	40.3	39.2	18.1
Max Free Yield)							
Oil Content w% of Product	80.2	75.9	91.3	94	89.8	63.4	98

Typical results attained when it is desired to
attain product of high Reactor Yield may be as follows:

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TABLE

Conditions	A Unrefined Minas 7 Distillate	B Unrefined Minas 8 Distillate	C Solvent Ref. Minas 8 Distillate	D Slack Wax 20	E Slack Wax 40	F Petrolatum	G Soft Wax
Reactor Temp, F	800	801	775	750	751	801	750
Reactor Pressure, psig	995	993	998	1004	1000	998	1006
Space Velocity, LSHV	0.54	0.53	0.53	0.58	0.58	0.55	0.49
Test							
Viscosity, SUS @ 100F	65	73	81	89	137	165	85
Viscosity Index	131	144	139	151	172	171	133
Pour Point, F	95	90	85	95	120	95	70
Reactor Yield, Wt% (700+F Wax Free Yield)	31.2	41.4	44.0	56.9	50.3	39.2	52.4
Oil Content w% of product	65.7	66.9	72.2	77.8	61.8	63.4	83

From the above Table, it is apparent that it is possible to prepare a low pour point product which is characterized by satisfactory viscosity and viscosity index. It is also possible to operate in manner to obtain im-

proved Reactor Yield.

It is a feature of the process of this invention that the high viscosity index product recovered by treating e.g. a slack wax is typically characterized as follows:

- (i) decrease in wax content from a charge value of typical 85-90w%, say 90w% to a product wax content of 5-85w%, say 20-25w% at optimum yield, and
- (ii) decrease in Pour Point from a charge value of typically $\geq 120^{\circ}\text{F}$ to a product Pour Point as low as 25°F , and typically $40\text{-}45^{\circ}\text{F}$.

It is a feature of the process of this invention that the product recovered by treating high wax distillate charge or a high-wax-content non-lube crude charge (such as a Minas) is characterized by:

- (i) increase in viscosity index from a charge value of typically 120-130, say 125 to a product viscosity index of 130-150, say 140;
- (ii) decrease in wax content from a charge value of typically 45w% to a product wax content of 10-40, say 20w%; and
- (iii) decrease in Pour Point from a charge value of typically $\geq 120^{\circ}\text{F}$ to a product Pour Point of $25^{\circ}\text{F}\text{-}90^{\circ}\text{F}$, say 40°F .

It is also a feature of the process of this invention that the high viscosity index product recovered by treating petrolatum is characterized by:

- (i) increase in viscosity index from a charge value of 130-150, say 140 to a product viscosity index of 155-190, say 170 (waxy oil basis);

- (ii) decrease in wax content from a charge value of 80-90w%, say 90w% to a product wax content of 25-75w%, say 35w%; and

- (iii) decrease in Pour Point from a charge value of $\geq 120^{\circ}\text{F}$ to a product Pour Point of $80^{\circ}\text{F}\text{-}120^{\circ}\text{F}$.

It is also a feature of the process of this invention that the product recovered by treating a soft wax (obtained from deoiling of slack wax to make hard wax - the soft wax containing a substantial portion of oil) is characterized by:

- (i) decrease in wax content from a charge value of 30w%-50w%, say 40w% to a product wax content of 2w%-28w%, say 20w%; and

- (ii) decrease in Pour Point from a charge value of $90^{\circ}\text{F}\text{-}120^{\circ}\text{F}$, say 110°F to a product having a Pour Point of $0^{\circ}\text{F}\text{-}90^{\circ}\text{F}$, say 70°F .

It will be apparent that the undewaxed products of the process of this invention may be improved generally with respect to Pour Point and wax content or Viscosity Index - depending upon the feed used. When it is desired to utilize product as a lube oil stock, it is highly desirable to thereafter subject the stock to solvent refining and dewaxing or catalytic dewaxing in order to obtain a product of sufficiently low wax content to attain the desired Pour Point. It is a feature of this process that in the case of some of the charge stocks (such as petrolatum or slack wax), it is found that it is possible to carry out solvent dewaxing on the treated products since a portion of the wax has been converted to oil and the oil content is now within the operating range of the solvent dewaxing operation. Previously it was not found to be economically feasible to subject such stocks to solvent dewaxing. The solvent dewaxed material may be solvent extracted to effect stabilization. Alternatively the product may be subject to solvent refining and catalytic dewaxing (in either order) and/or to high pressure stabilization.

It is a particular feature of the process of this invention that it is possible, by use of non-noble metal catalyst, to process sulfur-containing feedstocks without the need to employ a guard bed as is required by some prior art techniques.

It is also a particular feature of the process of this invention that (unlike prior art treating processes) it is possible, by use of a two-reactor train having a second reactor temperature about $100^{\circ}\text{F}\text{-}300^{\circ}\text{F}$, say 200°F lower than the temperature of the first (the second reactor typically being at $500^{\circ}\text{F}\text{-}600^{\circ}\text{F}$, say 550°F) to attain product unexpectedly characterized by substantially improved ultraviolet light (UV) stability. This increase in UV stability may be by a factor of as much as ≥ 10 and commonly by as much as 8-15 days. Prior attempts to hydrocrack and stabilize in a single train system without intermediate separation (i.e. fractionation or flashing to remove light gases such as hydrogen, hydrogen sulfide, or ammonia) prior to stabilization have not permitted attainment of product of significantly improved UV stability. Note e.g. Example XX-XXV infra.

In practice of the process of this invention, use of, higher pressures (e.g. \geq ca 1500 psig) within the operating range permits attainment of substantially improved UV stability - i.e. by a factor of three or more.

It is particularly surprising to be able to attain product oils which are characterized by such high viscosity index at such high reactor yield by use of a non-noble Group VIII catalyst. Prior art processes are particularly characterized by either lower Reactor Yield or by the fact that they require more restrictive feedstock or require feed hydrotreating to remove sulfur. It is a particular feature of the process of this invention that it is possible to improve the properties of a wide range of feedstocks - ranging from wax distillates to slack waxes without

hydrotreating of the feed to remove sulfur and nitrogen compounds.

The invention will now be further described by reference to the following non-limiting Examples.

EXAMPLES

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EXAMPLE I

In this Example, which represents the best mode presently known of carrying out the process of the invention, the hydrocarbon charge is a slack wax 20 characterized by the following properties.

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TABLE

Property	Value
- Wax Content (ASTM D-721) w%	89.1
- Oil Content w%	10.9
- Pour Point °F	≥ 120°F
- Viscosity cST @ 100°C	5.3

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This hydrocarbon charge is unsuitable for use as a lube oil stock because inter alia both the wax content and the Pour Point are undesirably high.

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In this Example the catalyst is prepared by mulling together equal parts by weight of the Pural SB brand (of Condea Chemie) boehmite alumina and the Versal 250 brand (of Kaiser Aluminum and Chemical) pseudo-boehmite alumina. Water is added to yield a mixture containing 58w% thereof as mixing is continued to give an extrudable mass. Extrudate (cylinders of 0.07 inch diameter) is dried overnight at 125°C and calcined at 670-700°C to yield product characterized as follows:

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TABLE

SiO ₂ %	20
A ₁ ₂ O ₃ %	80
Surface Area m ² /g	243
Total Pore Volume cc/g	0.66
Crush Strength 1bs	15
Diameter Inches	0.063

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An aqueous solution is prepared containing 1746.3g of ammonium metatungstate and 1996.4g of nickel nitrate hexahydrate and 295g of aqueous hydrofluoric acid with mixing. The resulting solution is diluted with distilled water to a total volume of 3150 cc. This solution is impregnated onto 4500g of calcined extrudate supra. The so-loaded composition is dried overnite at 125°C and calcined at 500°C for one hour. Product catalyst is characterized as follows:

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TABLE

5	Nickel	6%
10	Tungsten	19%
	Fluorine	2%
	SiO ₂	13.5%
15	Surface Area m ² /g	152
	Total Pore Volume cc/g	0.42
	Crush Strength lbs	20
	Diameter inch	0.063

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Wax conversion is carried out at 750°F and 1004 psig and LHSV of 0.58 on slack wax 20 charge (- see column D of Table supra).

Hydrogen (100% pure) feed rate is 2500 SCFB. Operation is carried out in liquid phase in a single reactor containing a fixed bed.

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Product lube base oil is characterized as follows:

TABLE

25	Viscosity, SUS @ 100°F	89
	Viscosity Index	151
	Pour Point °F	95
	Reactor Yield w% (700+°F Wax Free Yield)	56.9

30

From the above Table, It is apparent that the Pour Point has been decreased from ≥ 120°F down to 95°F; and the Reactor Yield is 56.9w%. (It should be noted that subsequent processing including dewaxing will decrease the Pour Point to even lower levels).

Product may be recovered and distilled to yield clean by-products. Typical values for these fractionation by-products (including naphtha and top quality kerosene cuts) may be as follows:

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Product is recovered and distilled to yield clean by-products including a naphtha (3.7w% of the feed) and a top quality kerosene (5.3w% of the feed).

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TABLE

		Cut	
	Property	Naphtha	Kerosene
5	RI @ 70°C	1.4010	1.4180
10	API Gravity	55.9	49.6
15	Flash (COC) °F	105	200
20	ASTM Color	< 1.0	< 1.0
25	Smoke Point °F	33	33
30	Freeze Point °F	- 100	- 60.7
35	Aniline Point °F	155	175
40	Hydrogen w%	14.90	14.75
45	Cetane No.	43.4	54
50	IBP °F	220	359
55	5%	258	385
60	50%	328	442
65	95%	384	499
70	EP	400	514

Distillate also includes a 500°F-600°F liquid cut (5.3w% of the feed) which is suitable for use in specialty applications (e.g. a specialty lube oil).

TABLE

	Property	500°F-600°F Cut	Value
35	Flash, UC °F		280
40	Vis., 40°C, cSt		3.74
45	Vis., 100°C, cSt		1.42
50	Vis., 100°F, SUS		40
55	Pour Point °F		- 25
60	Dielectric Bkd, V		39,500
65	Distillation, ep °F		627
70	UV Absorbance, millimicrons		
75	280-289		2.25
80	290-299		1.59
85	300-359		0.55
90	360-400		0.06

Distillate also includes a 600°F-700°F liquid cut (8.5w% of the feed) as follows:

TABLE

600°F-700°F CUT		
	Property	Value
5	Gravity, API	43.4
	Flash (COC) °f	325
10	Vis., 40°C, cSt	6.94
	Vis. SUS @ 100°F	50
	Unsulfonated Residue, w%	100
15	Pour Point °F	30
	Distillation ASTM-D2887	
20	IBP °F	579
	5%	603
	10%	613
	50%	671
25	90%	716
	95%	722
	EP	775

30 Distillate also includes the desired 700°F+ lube cut (73.1w% of feed ; 56.9w% on wax-free basis) suitable for use as a lube oil base stock after additional processing as follows:

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TABLE

700°F CUT		
	Property	Value
5	Gravity API	39.2
10	Flash (COC) °F	440
15	Vis, 65.6°C cSt	9.70
20	Vis, 100°C cSt	4.65
25	Vis SUS @ 100	109
30	VI	145
35	Wax Content w%	13.8
40	Pour °F	45
45	ASTM Distillation	
50	IBP °F	714
55	5%	756
60	10%	768
65	50%	831
70	90%	921
75	EP	1009

It is apparent that the process of this invention permits conversion of a wide range of feedstocks to a product lube base oil characterized inter alia by a high viscosity index, a substantially decreased wax content, and a substantially decreased Pour Point.

EXAMPLES II-IV

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In Examples II-IV, the procedure of Example I is followed except that the reactor pressure is 1500 psig. The catalyst of Example II is the same as that of Example I. The catalyst of Example III is a commercially available prior art catalyst containing 3w% nickel and 13w% molybdenum on gamma alumina. Surface Area is 162 m²/g. Pore Volume is 0.47 cc/g. Compacted bulk density is 52.5 lbs/ft³.

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The catalyst of Example IV is another commercially available catalyst; it contains 5w% nickel and 15.5w% molybdenum on Y-zeolite. Compacted bulk density is 49.9 lbs/ft³. Crush strength is 30 lbs. Catalyst particles are cylinders 0.3 inches long.

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The reactor temperature in Example II is 750°F; in Example III it is 800°F; and in Example IV it is 550°F. In Examples II-IV, reactor pressure is 1500 psig.

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The results are as follows:

TABLE

Finished Base Oil			
Example	Visc SUS 100°F	VI 0°F Pour	Reactor Yield W%
II	79	142	50.6
III	68	147	28.3
IV	109	123	15.7

From the above Table, it is apparent that the desired Reactor Yield attained in Example II is much higher

than (approximately twice) those of Examples III-IV. Reactor Yield of Example II at 750°F is better than that of Example III at 800°F or Example IV at 550°F. It is also to be noted that this unexpectedly high yield of high viscosity index oil is attained by operation at 750°F (Example II) which is 50°F lower than the temperature (800°F) of Example III.

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EXAMPLE V

In Example V, the procedure of Example I is followed except that the catalyst is a commercially available supported catalyst containing 6.5w% nickel, 3.4w% fluorine, and 19.4w% tungsten of Surface Area is 126 m²/g.

- 10 Pore Volume is 0.38 cc/g. Compacted Bulk Density is 62.4 lbs/ft³. Reactor temperature in Example V is 750°F and pressure 1000 psig.

TABLE

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Finished Base Oil				
Example	Visc SUS 100°F	VI (0°F Pour)	Reactor Yield W%	Pressure Psig
I	86	142	56.9	1000
V	79	142	50.6	1000

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From the above Table, it is apparent that practice of the process of this invention (Example I) to attain product dewaxed oil (DWO) of 142 VI may be achieved at a reactor yield of 56.9W%.

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EXAMPLES VI-XII

In this series of Examples, the charge stocks treated are those set forth following in the charge Stock Table:

TABLE

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Example	Charge Stock
VI	A - Unrefined Minas 7 Distillate
VII	B - Unrefined Minas 8 Distillate
VIII	C - Solvent Refined Minas Distillate
IX	D - Slack Wax 20
X	E - Slack Wax 40
XI	F - Petrolatum
XII	G - Soft Wax

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Treating is carried out in accordance with the procedure of Example I - but in order to attain low Pour Point, the conditions of operation are: temperature 771°F, pressure 997 psig, and LHSV 0.53.

45 The product oils were tested to determine the viscosity (SUS) 100°F, the Viscosity Index (VI), pour point, and calculated 700+F Wax-Free Lube Yield w%.

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Example	Temp °F	Press psig	Viscosity (SUS@100°F)	VI		Pour Point °F	Reactor Yield %
				VI	VII		
VI	826	996	58	131	25	23.3	
VII	826	997	66	145	25	24.2	
VIII	800	998	66	130	20	29.3	
IX	771	997	66	135	25	40.4	
X	775	1001	89	144	55	40.3	
XI	801	998	165	171	95	39.2	
XII	775	1008	61	112	0	18.1	

TABLE

From the above Table, it is apparent that it is possible to attain product of high viscosity index with desirably reduced Pour Point at high yield. In the case of Example X slack wax 40 (a high viscosity charge stock of high wax content), the wax content has been reduced from 87w% down to 9.5 w%; and thus this treated high Pour Point charge can readily be dewaxed to yield a high quality, low Pour Point, low wax content lube oil stock. It should be noted that the viscosities set forth in the above Table are measured on the hydrotreated (non-

dewaxed) product which contains material boiling both above and below 700°F. Further dewaxing and fractionation gives the above-reported Reaction Yields of the 700°F fraction and desirably increases the viscosity of the product to within the desired range of SNO-100 and SNO-200 oils; and the viscosity index will increase further - above the levels presented in the Table.

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EXAMPLES XIII-XIX

It is thus a feature of the process of this invention that it is possible to operate in manner (note Examples VI-XII supra) to attain product characterized by low Pour Point. When conditions (including economic factors) dictate that operation be carried in a manner to attain high reactor yield for a given charge, this may be readily accomplished. For each charge stock, the conditions which give high Reactor Yield include operation at a temperature of about 25°F lower than the temperature at which low Pour Point is attained (and at essentially the same pressure and space velocity LHSV). This may be noted from the following Examples XIII-XIX wherein the conditions of Examples VI-XII are duplicated except for temperature.

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TABLE

Example	Temp °F	Press PSIG	Viscosity SUS @ 100 °F	VI		Pour Point °F	Reactor Yield
XIII	800	995	65	131	131	95	31.2
XIV	801	993	73	144	144	90	41.4
XV	775	998	81	139	139	85	44.0
XVI	750	1004	89	151	151	95	56.9
XVII	751	1000	137	172	172	120	50.3
XVIII	801	998	165	171	171	95	39.2
XIX	750	1006	85	133	133	70	52.4

55 From the above Table, it will be apparent that a lowering of temperature of operation by about 25°F will permit attainment of improved Reactor Yield. For Example, a comparison of Example VI (Run at 826°F) with Example XIII (Run at 800°F) shows increase in Reactor Yield from 23.3w% to 31.2w% - by a factor of about 34%.

EXAMPLES XX-XXV

In this series of Examples, Slack Wax 20 was charged to the reactor containing the catalyst at the conditions noted in the Table below. Examples XXII-XXIII were carried out in two stage operation with a temperature of the first stage of 700°F and the second stage of 550°F. Example XXIV was also carried out in two stages at temperatures of 700°F and 500°F respectively. LHSV in all cases was about 0.5 volumes per volume of catalyst. Catalyst D of the Table supra was employed in Examples XXII - XXIV. Catalyst A was employed in Examples XX, XXI, and XXV.

TABLE

10	Example	Stability Days	Reactor Yield W%	Reaction Conditions	
				Temp °F	Pres. psig
15	XX	3	50.1	750	1500
	XXI	2	49.1	750	1000
	XXII	11+	45.1	700/550	1000
20	XXIII	14+	47.8	700/550	1500
	XXIV	18+	42.9	700/500	2500
	XXV	35+	43.8	770	1000

Reactor Yield is the product of the 700°F bottoms yield in w% times the oil content weight fraction.

From the above Table, it is apparent that high Reactor Yield is attained in all runs. Operation using two stages (Examples XXII-XXIV) permits attainment of product characterized by particularly high UV Stability. In the case of Example XXV, it should be noted that the values reported are those attained after the product of this invention was solvent refined; and this resulted in a significant increase in UV Stability.

It may also be noted that although the products of Examples XX-XXI are of course characterized by high Reactor Yield, improved Pour Point, decreased Wax Content, and high Viscosity Index, the lower UV stability of these products may readily be improved by solvent refining or hydrofinishing.

Prior art hydrocracking processes which attempt to prepare stabilized product find it necessary to utilize a separate hydrogenation step or a separate solvent extraction step. Although it is possible to effect further stabilization of the products of the process of this invention by solvent extraction, it is unexpectedly found that the use of a second lower temperature hydrogenation/stabilization improves UV stability and eliminates the need (as is taught by the prior art) for intermediate separation and purification steps between the first conversion operation and the stabilization operation.

Although this invention has been illustrated by reference to specific embodiments, it will be apparent to those skilled in the art that various changes and modifications may be made which clearly fall within the scope of the invention.

Claims

- 45 1. A process for converting a waxy hydrocarbon charge of high Pour Point and containing sulfur and paraffins to a hydrocarbon product of reduced Pour Point and high viscosity index which comprises maintaining a bed of sulfur-tolerant supported catalyst comprising a non-noble Group VIII metal, a Group VI B metal, optionally phosphorus and halogen having a Total Surface Area of 100-250 m²/g and a pore size distribution as follows:

Pore Size	Pore Volume cc/g
< 100 Å	0.20-0.50
100-160 Å	0.01-0.05
> 160 Å	0.01-0.10

and a Pore Mode of 60Å-100Å diameter;

passing waxy hydrocarbon charge of high Pour Point and containing sulfur and paraffins to said bed of catalyst;

5 maintaining said bed of catalyst at wax conversion conditions including temperature of 288-482°C (550°F-900°F), pressure of 2-33 kPa (300-5000 psig), space velocity LHSV of 0.1-10, and hydrogen feed rate of 88-1800 m³/m³ (500-10,000 SCFB) thereby converting said waxy hydrocarbon charge to a hydrocarbon product, of reduced Pour Point and high viscosity index; and recovering said hydrocarbon product.

- 10 2. A process as claimed in Claim 1 wherein the catalyst comprises 2-10 wt% of a non-noble Group VIII metal, 5-30 wt% of Group VI B metal, 0-2 wt% phosphorus and 0-10 wt% halogen.
- 15 3. A process as claimed in Claim 1 wherein said wax conversion conditions include a temperature of 343°-454°C (650°F-850°F) and a pressure of 6895-17237.5 kPa g.p. (1000-2500 psig).
- 20 4. A process as claimed in Claim 1 wherein said catalyst contains support bearing 3-8wt% non-noble Group VIII metal, 10-25wt% Group VI B metal, and 0.5-10wt% halogen.
- 25 5. A process as claimed in any one of Claims 1 to 4 wherein said waxy hydrocarbon charge has a Pour Point of 27-50°C+ (80°F-120°F+).
- 30 6. A process as claimed in Claim 5 wherein said waxy hydrocarbon charge is a slack wax.
- 7. A process as claimed in Claim 5 wherein said waxy hydrocarbon charge is the soft wax obtained from de-oiling of (i) slack wax, (ii) high wax-content distillates or (iii) deasphalted oil.
- 35 8. A process as claimed in Claim 5 wherein said waxy hydrocarbon charge is a solvent extracted distillate or a solvent extracted deasphalted oil.
- 9. A process as claimed in any one of Claims 1 to 4 wherein the hydrocarbon product is subjected to one or more further treatments selected from solvent extraction, solvent dewaxing, solvent refining, catalytic dewaxing and high pressure stabilisation.
- 40 10. A process for converting a waxy hydrocarbon charge of high Pour Point and containing sulfur and paraffins to a hydrocarbon product of reduced Pour Point and high viscosity index which comprises maintaining a first and a second bed of sulfur-tolerant supported catalyst comprising a non-noble Group VIII metal, a Group VI B metal, optionally phosphorus and halogen having a Total Surface Area of 100-250 m²/g and a pore size distribution as follows:

Pore Size	Pore Volume cc/g
< 100 Å	0.20-0.50
100-160 Å	0.01-0.05
> 160 Å	0.01-0.10

45 and a Pore Mode of 60Å-90Å diameter;

passing waxy hydrocarbon charge of high Pour Point and containing sulfur and paraffins to said first bed of catalyst;

50 maintaining said first bed of catalyst at wax conversion conditions including temperature of 288°-482°C (550°F-900°F), pressure of 2-33 kPa g.p. (300-5000 psig), space velocity LHSV of 0.1-10, and hydrogen feed rate of 88-1800 m³/m³ (500-10,000 SCFB) thereby converting said waxy hydrocarbon charge to a first hydrocarbon product, of reduced Pour Point and high viscosity index;

recovering said first hydrocarbon product;

passing said first hydrocarbon product to said second bed of catalyst;

55 maintaining said second bed of catalyst at temperature 55°-167°C (100°F-300°F) lower than the temperature of said first bed, at pressure of 2-33 kPa g.p. (300-5000 psig), space velocity LHSV of 0.1-10, and hydrogen feed rate of 88-1800 m³/m³ (500-10,000 SCFB) thereby converting said first hydrocarbon product to a second hydrocarbon product particularly characterised by improved stability to ultraviolet light; and recovering said second hydrocarbon product.



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(54) Wax conversion process.

(57) Hydrocarbon lube boiling range stock of high Pour Point may be catalytically hydrotreated to yield a product of high viscosity index and reduced Pour Point which is suitable as a lube base oil. The catalyst comprises a non-noble Group VIII metal, a Group VI B metal, optionally phosphorus and halogen. The catalyst is used at 280°-500°C, a pressure of 2-33 kPa gauge, LHSV of 0.1-10 and hydrogen feed rate of 88-1800 m³/m³.

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EUROPEAN SEARCH REPORT

Application Number

EP 92 30 9289

DOCUMENTS CONSIDERED TO BE RELEVANT									
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.)						
A	GB-A-1 065 205 (SHELL) * claims 1-13 * * page 3; table 1 * ---	1,2,3,7, 10	C10G45/60 C10G65/04						
A	DE-B-1 000 017 (DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ) * claims 1,3 * * column 3, line 6 - line 31 * ---	1,3,10							
A	US-A-3 684 695 (SHELL) * claims 1,2,3,6,8,9 * * column 5, line 3 - line 26 * ---	1,2,3,4, 7,9							
A	EP-A-0 335 583 (ENGELHARD) * claims 1,2,8,9,11,25,26,27 * * page 7, line 55 - line 59 * * page 8, line 29 - line 38 * * example 1B * ---	1,2,3,4, 9,10							
A	FR-A-2 306 254 (SHELL) * claims 1,4,5,6,7,8 * * page 3, line 25 - line 31 * * page 5, line 4 - line 17 * -----	1,2,3,4, 7,9,10	TECHNICAL FIELDS SEARCHED (Int. CL.) C10G						
<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 34%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>19 APRIL 1993</td> <td>OSWALD DE HERDT</td> </tr> </table>				Place of search	Date of completion of the search	Examiner	THE HAGUE	19 APRIL 1993	OSWALD DE HERDT
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